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Summary

The optical and electronic properties of conjugated polymers (CPs) have been intensively studied in the last two decades, stimulated by the potential applications in large-area displays, photovoltaics, radio-frequency identification tags, gas sensors and transistors *etc*. Their ease of processing, light weight, the possibility to quickly cover large areas via cheap printing or coating techniques and their mechanical flexibility make them ideally suited for large-area applications. The delocalized π-electrons are responsible for the conductivity of CPs as a result from the alternation of single and double bonds. The charge carriers can hop between the conjugated segments of the chains assisted by the electric field with a hopping rate strongly depending on the energetic and structural disorder in CPs. The mobility of the charge carriers, being a measure of how easy charge carriers can move under an applied electric field, is of importance for the performance of electronic devices based on CPs. . However, due to impurities (defects, twists *etc*.) in polymer chains, leading to a limited conjugation length, the mobility of CPs is orders of magnitude lower as compared to inorganic semiconductors. It has been demonstrated that the mobility of the charge carriers in PPV derivatives at room-temperature is mainly governed by the density of charge carriers. Therefore, an efficient way for improving the mobility and conductivity is to enlarge the carrier density by doping the conducting polymer. Another advantage of electrical doping is that it not only enhances the charge transport, but also the injection of charges, The charge injection is governed by the presence of an injection barrier, which originates from the energy offset between the Fermi level of metal electrode and the transport level of the CP. Unfortunately large injection barriers are in many cases inevitably present e.g. for fluorine based polymers with a deep-lying HOMO level it is very difficult to find a suited anode. However, by addition of doping a strong band bending at the metal/polymer interface is induced, leading to a lowering of the charge injection barrier. For sufficiently high doping the band bending is confined to such a small region that the charge carriers can effectively tunnel through it, leading to the formation of an Ohmic contact. In silicon technology the implantation of doping is used to create Ohmic contacts.

In organic semiconductors the concept of doping has first been developed for organic small molecules. Thin films of these small molecules are deposited by thermal evaporation. A dopant molecule is then co-evaporated with the host from another source. In this way, a

homogeneous distribution of the doping in the host is achieved. However, conjugated polymers are deposited from solution. Adding a dopant to the solution easily leads to charge transfer and aggregation already in the solution, making processing of thin films from such a solution impossible. In this thesis, we address controllable doping of conjugated polymers using molecular dopants and examine how the charge transport in *p*- and *n*-type doped CPs behaves upon doping. Also stressed in this thesis is the tunability of the charge injection barriers through doping for blocking contacts (e.g. Schottky diodes).

As the intrinsic hole transport in PPV derivatives is well understood, we first examine *p*-type doping of MEH-PPV by studying the electronic properties of p-type doped diodes as discussed in *Chapter 2*. For the doping to become efficient, the energy levels between the host and the dopant should be matched. Therefore as a dopant the molecule F4-TCNQ is chosen, which is a strong acceptor with a deep LUMO of ~5.2 eV. Due to a relatively low dielectric constant of CPs the electrostatic Coulombic forces are strong. Therefore, when doping is introduced the holes from the F4-TCNQ acceptor are difficult to be separated from the negatively charged acceptors, leading to undesired aggregation in the solution. We experimentally overcome this issue by adding a certain amount of polar solvent and the *p*-type doped MEH-PPV film can then be spin-coated with satisfying smoothness. The hole current in diodes upon doping is found to be Ohmic under low electric field where the background carrier density p_0 from doping is dominant. Under high electric field the amount of holes injected from the contacts strongly exceeds the back groundd density of holes arising from doping (p_0), and the transport becomes space-charge limited. The important parameter p_0 can be determined by modeling of the current-voltage characteristics, taking into account that not only the amount of charge carriers but also the mobility is increased by doping. The background hole density is verified by impedance measurements on Schottky diodes. This confirmation also demonstrates that the mobilities in undoped and doped MEH-PPV are intrinsically equal, the enhancement of μ_p is just due to the enlarged carrier concentration. Without considering the density-dependence of the mobility the density p_0 as caculated from the current-voltage characteristics would be overestimated by an order of magnitude.

The mobility of doped MEH-PPV as a function of temperature (T) has been investigated as addressed in *Chapter 3*. The density-dependent mobility model consistently describes the T-dependence of the hole transport in undoped diodes However, assuming a temperature independent p_0 always leads to an overestimation of the T-dependence of the mobility in doped diodes. By assuming a field-assisted ionization of the dopant, given by $\sim e^{\gamma\sqrt{F}}$, the T-dependence of the mobility upon doping can be correctly described. The activation E_A of the

mobility, being a measure of the energy distance between the transport level and equilibrium level in the Gaussian DOS decreases from 0.45 eV to ~0.25 eV after doping due to an enhanced ionization. In addition, the activation energy of p_0 doping is separately measured by impedance analysis. The small activation energy of a few tens of meV is neglegible in the description of the charge transport propeties.

The capability of doping to improve the charge injection in CP is described in *chapter 4*. Using the F4-TCNQ acceptor a tunable charge injection barrier controlled by the doping concentration in rr-P3HT based Schottky diodes is demonstrated. A strong increase of the injection limited current is observed for already moderate doping levels of 10^{17} cm^{-3}, that can not be attributed to barrier lowering due to image forces. The reduction of the injection barrier height can be estimated from the rectification ratio of the *J–V* characteristics, showing a linear decrease with increasing the mobile hole densities. This linear decrease can be explained by the presence of a F4-TCNQ surface layer.

Both in LEDs and solar cells a balanced charge transport between electrons and holes is required for realizing high performances. However, in many CPs the electron transport is strongly hindered by traps, probably impurties that capture free electrons. In *Chapter 5*, we use an efficient donor molecule namely the DMC to *n*-type dope MEH-PPV and evaluate its effect on the electron transport. We demonstrate that the electron transport in MEH-PPV is limited by deep traps that are exponentially distributed in energy. By applying *n*-type doping these traps can be filled with electrons and therefore they are electrically made inactive, enabling the measurement of trap-free electron transport in MEH-PPV diodes. It is demonstrated that the mobility and microscopic origin of the electron and hole transport in conjugated polymers as MEH-PPV are identical, showing that the charge transport is intrinsically balanced.

After electrically characterizing the charge transport in molecularly doped diodes, the effect of *n*-type doping on the photoluminescence is investigated for a more in-depth understanding, as discussed in *Chapter 6*. For *n*-type doping, we show an evident PL quenching in MEH-PPV, which can be attributed to the trapping of photo-generated holes by electrons that fill the traps after ionization of the dopant. The remaining electron is then captured by the now empty trap, resembling non-radiative Shockley-Read-Hall recombination. This additional recombination leads to a decrease of the lifetimes of the PL with increasing doping concentration.

In conclusion, the application of *p*- and *n*-type doping gives rise to strongly enhanced charge transport properties in conjugated poymers. The background hole density and the total ionized electron density from the dopants are analytically determined both from current-voltage measurements and impedance measurements. A controllable doping not only leads to new insights into the electronic properties of organic devices but can also be applied to the improvement of charge transport and injection in devices based on conjugated polymers as PLEDs.